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VULCANIZING SYSTEMS FOR RUBBER

M. OLŠOVSKÝ[1], V. MACHO[1], P. GÁŠEK[2]

[1] Departent of Chemistry and Technology of Rubber, Faculty of Industrial Technologies TnUAD in Púchov, I. Krasku 491/30, 020 01 Púchov, Slovakia, e-mail: olsovsky@fpt.tnuni.sk
[2] Matador, j. s. c., T. Vansovej 1054/45, 020 32 Púchov, Slovakia, e-mail: peter.gasek@matador.sk

ABSTRACT: Following the results presented authors inform on preparation of ternary or multicomponent copolymer of sulfur prepared by addition or polyaddition of cyclooctameric sulfur to low molecular weight polybutadiene (Krasol) and with mixture of unsaturated carboxylic acids from rapeseed oil similarly as at substitution of polybutadiene with mixture of dimers of pyrolitic C_5-fraction. The most appropriate content of organic fraction in copolymeric sulfur is 10 – 30 wt %. The temperature of copolymerization is 125 – 150°C.
Vulcanizing characteristics of rubber mixtures and physical-mechanical properties of cured rubbers prepared with above mentioned ternary or multicomponent copolymers of sulfur and with commercial sulfur (Crystex OT 33) as well are stated. Vulcanized rubbers prepared from ternary or multicomponent copolymers of sulfur containing sulfur: C_5 – C_{10} diene fraction : low molecular weight polybutadiene: acids from rapeseed oil in weight ratio 10:1:3 achieve at the equal sulfur content comparable – or in some parameters (strength, strength after aging and modulus 300) better – physical-mechanical parameters then that prepared with polymeric sulfur.

KEY WORDS: copolymer of sulfur, vulcanizing agent, conjugated dienes, low molecular polybutadiene, rubber

1. INTRODUCTION

Copolymers of sulfur dioxide and/or carbon monoxide and olefins, especially ethylene, can be made by contacting these monomers with a combination of selected strong Lewis acid and a selected metal or a compound of a selected metal. The resulting polymers, which are often alternating copolymers, are useful as vulcanizing agents [1].

Reaction products of sulfur with an unsaturated reactant selected from d-limonene, 5-ethylidene-2-norbornene, styrene, and dicyclopentadiene, reacted at a temperature above the melting point of sulfur and below 159 °C until chemically combined, then further reacted above the melting point of sulfur until solidified [2]. The resulting products serve as vulcanizing agents when compounded with rubber. The unvulcanized rubber compounds exhibit less blooming and better adhesion to a variety of substrates than rubber compositions compounded with soluble or insoluble sulfur. Vulcanizates containing the present compositions and a method for increasing the adhesion of rubber to a substrate during a vulcanization process are also disclosed [2].

Superior vulcanization agents for rubber are prepared by reacting sulfur with at least one olefin at 120 – 200 °C in an aqueous reaction media with agitation [3, 4]. In one embodiment, the vulcanization agent comprises a sulfur/olefin adduct having from 39 - 46 wt. % of elementary sulphur.

The copolymeric sulphur was prepared by copolymerization reaction of cyclooctameric sulfur (from natural granular sulphur or powdered sulfur from Claus process) mainly with dimers of dienes of C5 fraction, with C20 – C24 1-alkenes, and with rapeseed oil containing mainly unsaturated carboxylic acids and their methylesters [5, 6]. Inert nitrogen atmosphere, continuous stirring, temperature from 125 - 150 °C and reaction time were 4 hours. Mechanical properties of vulcanizates

with sulfur copolymers with dienes and olefins are similar to properties of vulcanizates with polymeric (insoluble) sulfur. In the case of copolymeric sulfur with dimers of dienes C5 the smelling dienes are released and some mechanical property values of copolymeric sulfur are lower. Copolymers of sulfur with unsaturated acids from rapeseed oil, as well as with its methylesters (up to 10 wt. %), which have application as vulcanization agent of unsaturated rubbers based mixtures, have vulcanization parameters as well as mechanical properties comparable with polymeric sulfur. In addition, they are easily blended into the rubber mixture.

2. EXPERIMENTAL

Organic acids (mixture of higher fatty acids of rapeseed oil); producer: Polychem, Prievidza; approximate content of carboxylic acid (in wt. %): palmitic acid C_{16} = 4; stearid acid C_{18} = 2; oleic acid C_{18} = 60; linoleic acid = 22; linolenic acid C_{18} = 10; eicozanic acid C_{20} = 2; erucic acid C_{22} = 1; saponifying number = 204.0 mg KOH/g; acidity number = 191.3 mg KOH/g; iodine number = 98.5 g I_2/100 g material; content of water by Fischer = 0.48 wt. %.

Distillation residue of pyrolytic C_5 fraction from pyrolysis of petroleum fractions; producer: Slovnaft – MOL, Bratislava; bromine number = 254.3 g Br_2/100 g material; prevailingly mixture of unsaturated polyenes C_5 with boiling temperature = 40 – 80 °C / 6.7 kPa.

Sidewall mixture (prepared 1. step); composition: IR, SBR, BR, carbon black (type N 330 and N 550), plasticator (Furex 433)

Accelerator of rubber vulcanisation – Sulfenax CBS/MG (N-cyclohexyl-2-benzothiazolyl sulphenamid); producer: Istrochem Bratislava; purity = 96.7 wt. %; ash = 0.1 wt. %.

Vulcanization retarder – Duslin G80 (N-cyclohexyl thioftalimide); density 1150 kg/m^3; melting point = 80 °C; with effective matter content = 79.5 wt. %; wax = 18.5 wt. %; ash = 0.1 wt. %.

Sulphur N (mixture of polymeric sulphur in cyclooctameric); producer: Istrochem Bratislava; with the content of polymeric sulphur = min. 48 wt. %; content of oil: 20 % wt.

3. PREPARATION OF COPOLYMERIC SULPHUR

In connection with the very easy preparation of copolymeric sulfur [6] and also accessibility of raw materials and very good mechanical properties of prepared vulcanizates, we have decided for more detailed search of reaction conditions and tested different ratios of cyclooctameric sulfur.

Copolymeric sulphur has been prepared with cyclooctameric sulfur with dimers of dienes C5 fraction and organic acid (mixture of higher fatty acids of rapeseed oil). Ratio components of C5 fraction and organic acid were 1: 3. A content of sulfur was from 75 to 99 wt. % (Tab. 1).

We melting the reaction mixture for a period of 5 minutes, next the reaction mixture war rapidly mixed with mechanical stirrer in the inert atmosphere during 240 minutes. Reaction temperature was 128 ± 2 °C. After 15 minutes of the reaction time was formed homogeneous mixture. The final products were solid, dark and fragile. Then they were grind to dust with particle size under 0.071 mm.

Tab. 1: Contents of sulfur in samples

Sample	Contents of sulfur [wt. %]	Quantity samples in rubber mixture [phr]
1	75	2,65
2	78	2,56
3	90	2,50
4	95	2,37
5	98	2,32
6	99	2,28

4. PREPARATION OF RUBBER MIXTURES AND PROCESSING CHARACTERISTIC

We studied the efficiency of copolymeric sulphur as vulcanizing agent for sidewall mixture, which is utilized for production of sidewalls and clinchers of passenger car radial tyres. As comparable standard we have prepared mixture with polymeric sulphur (Sulfur N), which is commonly used as vulcanizing agent in the sidewall mixtures. The preparation of rubber mixtures was made by two-step mixing according Slovak standard STN 62 1425. In the second step of rubber mixture we tested samples as vulcanizing agent and another vulcanizing admixtures – accelerator (Sulfenax MBS) and inhibitor of overvulcanization (Duslin G80), which is used for the sidewall rubber mixture. The amount of sulfur in samples was calculated in order to achieve equal content of sulphur in the mixture as in the standard (Sulfur N). The exact amounts of individual components to the second step of the rubber mixtures mixing are in the Table 1.The mixing of the second step was made at temperature 75 °C of the open laboratory double-geared with friction 1:1.14. We made vulcanizing curves for all mixtures. All mixtures show very low reversion of vulcanizing curves. Individual vulcanizing characteristics were calculated from vulcanizing curves (Tab. 2). These vulcanizing curves are steeper in comparison with polymeric sulfur (sample 1). It shows that vulcanizing time is shorter about 3 minutes. We made vulcanizing characteristics of the rubber mixtures at 150 °C during 60 minutes of registration in vulcameter Monsanto. All vulcanizing curves of rubber mixtures have increasing torsional moment. The values of the vulcanizing parameters are comparable with parameters of rubber mixture with polymeric sulfur, which was chosen as reference material. From the comparison of the vulcanizing curves, respectively parameters are clear that vulcanization is faster (about 5 %) in comparison with the mixture with polymeric sulfur and also vulcanizing curves of mixtures are steeper than with polymeric sulfur (Tab. 2).

Tab. 2: Processing characteristic of rubber mixtures

	sulfur N	**1**	**2**	**3**	**4**	**5**	**6**
Viscosity Mooney (100 °C, 1+4, ML)	52,1	51,5	53,1	53,0	51,5	54,8	55,6
Scorch time, 120 °C [min.]	61,98	49,38	52,33	49,03	53,12	47,08	49,44
Vulcanization time [min.]	21	17	18	19	17	18	18
Blooming of vulcanizing agent [days]	40	25	24	22	23	20	17

5. DESIGNATION OF MECHANICAL PROPERTIES

Vulcanized mixtures in the forms of plates were stored 24 hours. Then we prepared with cutting the test specimen in the form of bothsides shovels for tensile tests. For hardness test specimen were in the form of rings and in the form of "graves" for designation of the tear strength. The cut samples were conditioned for at least 16 hours at examinational temperature and then we have determined mechanical properties. Measured values of mechanical properties are in the Table 3.

Tab. 3: Mechanical properties of vulcanizates

	sulfur N	**1**	**2**	**3**	**4**	**5**	**6**
Hardness [Sh A]	58,8	62,83	62,23	62,30	62,20	61,30	61,60
Rebiund resilience [%]	59,4	59,07	58,33	59,30	58,40	57,70	58,90
Strength [MPa]	18,62	17,73	18,87	17,05	18,51	18,38	18,52
Elongation [%]	441	407	341	451	359	377	432
Modulus 300 [MPa]	10,96	10,37	10,44	10,42	10,47	10,39	10,46
Tear strength 20 °C [kN/m]	51,74	60,10	58,21	55,13	56,00	59,26	54,36
Tear strength 90 °C [kN/m]	29,36	31,70	30,26	32,08	41,36	43,10	40,52

6. CONCLUSIONS

From the achieved results we can conclude that from the point of view of vulcanizing agent incorporation to rubber mixtures, copolymeric sulfur with 10 – 15 wt. % of organic portion is better incorporable than polymeric sulfur. At optimum amount copolymeric sulfur applied as vulcanizing agent regarding mechanical properties are comparable with polymeric sulfur (Sulfur N). However, evidently over performs the standard in tear strength at 20 °C and at 90 °C respectively. Also material hardness properties are better. The stability of rubber mixtures prepared with copolymeric sulfur is good from the point of view of "blooming". The "blooming" starts at storage after 17 - 22 days, and more intensive "blooming" appears after 25 - 35 days but in the case of polymeric sulfur (Sulfur N), however, it starts after 25 - 35 days. In case of cyclooctameric sulfur it is only 9 - 11 days [6].

Moreover, copolymeric sulfur accelerates vulcanization time about 5 %. Its utilization seems to be interesting from several points of view, as effective, safe, ecologically friendly and also potentially technically and economically available vulcanizing agent for vulcanization of unsaturated rubbers.

7. REFERENCES

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